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Formation and Photochemical and Thermal Reactions of Adduct between 1,2,5,3-Cobaltadithiazole and Dimethyl Acetylenedicarboxylate

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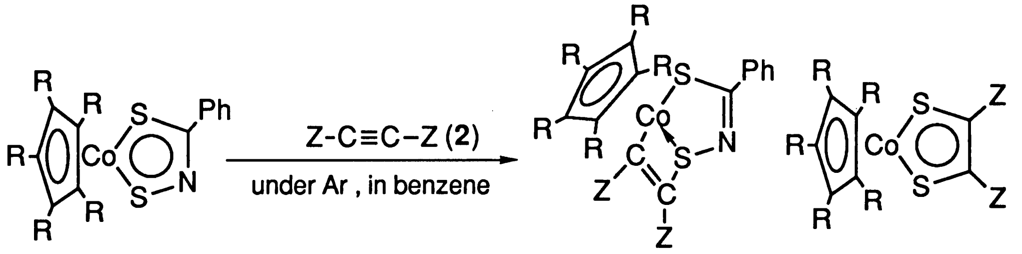
(η^5-Cyclopentadienyl or η^5-pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1**) reacts with dimethyl acetylenedicarboxylate (DMAD) to give the adducts in which Co and S of the 1,2,5,3-cobaltadithiazole ring in the cobalt complex are bridged by 1,2-dimethoxycarbonylethylene-1,2-diyl groups (**3a**: the complex having Cp and **3b**: the complex having Cp*). The sulfur atom adjacent to N is preferentially reacted. Photolysis of **3** gives 3,4-dimethoxycarbonyl-1,2,5-cobaltadithiolene (**4**) with the elimination of benzonitrile. In thermolysis in benzene, **3a** undergoes selectively the elimination of benzonitrile to give **4a**, while **3b** undergoes the elimination of either DMAD or benzonitrile to give **1** or **4**.

We have reported unique reactivities of the 1,2,5-cobaltadithiolene ring, which consists of a cobalt atom, two coordinated sulfur atoms, and two unsaturated carbon atoms.1) The ring is a conjugated system with 6 π elecrons and shows both aromaticity and unsaturation. Our studies on the reactivities of metalladithiolene ring in (η^5-cyclopentadienyl)(1,2-ethylenedithiolato)metal(III) (metal = Co or Rh) have revealed a variety of interesting addition and dissociation reactions which occur in the metalladichalcogenolene rings.1d) Insertion (addition) reactions between metal and sulfur are characteristic reactions for the metalladithiolene rings. Typical reactions are additions of alkylidenes by diazo compounds,2) addition of alkyne,3) and addition of quadicyclane.4) Recently we succeeded in the synthesis of a nitrogen-containing analog of cobaltadithiolene, 1,2,5,3-cobaltadithiazole, which is a novel metallacycle.5) The substitution of a nitrogen atom for a carbon atom may cause important changes in the physical and chemical properties of the metallacycle. In this paper we compare the reactivities of 1,2,5,3-cobaltadithiazole with those of 1,2,5-rhodiadithiolene in the reactions with dimethyl acetylenedicarboxylate.3)

(η^5-Cyclopentadienyl or η^5-pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1a or 1b**) (0.1 mmol) reacts with dimethyl acetylenedicarboxylate (DMAD, **2**) (0.4 mmol) at room temperature for 24 h. The single 1:1 adduct between cobaltadithiazole and dimethyl acetylenedicarboxylate was obtained in high yield in each case (70% for **3a** with cp and 99% for **3b** with Cp*).6) As byproducts, a small amount of (η^5-cyclopentadienyl or -pentamethylcyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III) (**4a** or **4b**) (yield of **4a**, 2%; yield of **4b**, 1%) and a trace amount of tetramethyl thiophene-2,3,4,5-tetracarboxylate were obtained.

The comparison of their NMR and MS values with those of the adduct between rhodiadithiolene and DMAD shows that the alkyne bridges between cobalt and S which is adjacent to N. The ^{13}C NMR of the adduct between a rhodiadithiolene (η^5-cyclopentadienyl)(1,2-dimethoxycarbonyl-1,2-ethylenedithiolato)-rhodium(III) and DMAD, the structure of which was determined by X-ray diffraction,[3b)] showed that the signal of the C adjacent to the bridged S appears at δ = 107.4 (up-shifted from δ = 134 for that of the free dithiolene) and that of the other C appears at δ =178.6 (down-shifted). The signal of of the C in the cobaltadithiazole ring in the adduct **3b** appears at δ = 203.4. This value is greater than δ = 184.3 of the free cobaltadithiazole. The down-shift indicates that the bridging occurs at the S atom away from the C atom, namely at the S atom adjacent to N.



1a: R = H
1b: R = Me

Z = COOMe

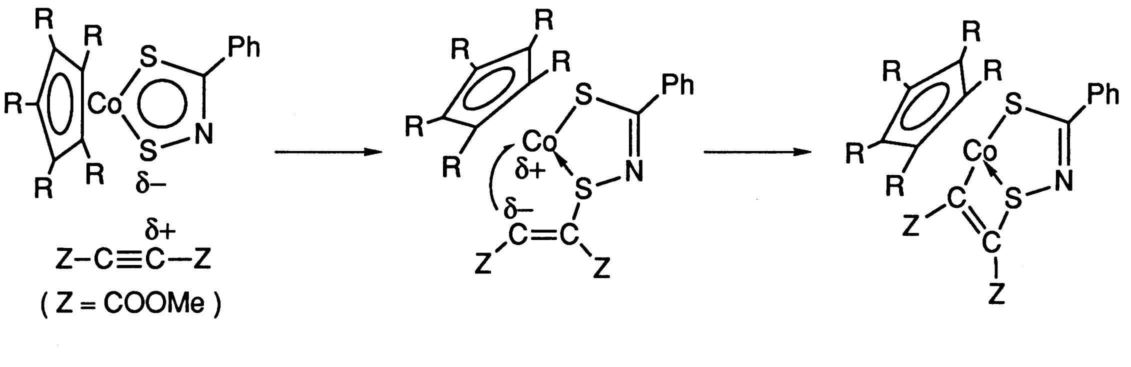
3a: R = H
3b: R = Me

4a: R = H
4b: R = Me

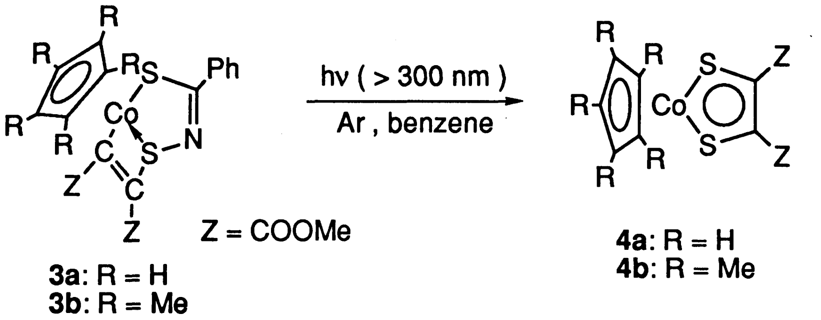
The addition reaction between Co and S occurs in the reaction with diazo compounds (the bridging by methylene).[2)] The addition of methylene is initiated by the attack of the negatively charged C of the 1,3-dipolar diazo compound to the positively charged central metal of the metalladithiolenes. The electron-richer diazo compounds react more easily.

In contrast to the addition of methylene, the addition of alkyne occurs only with electron defficient alkynes, DMAD and methyl acetylenecarboxylate to **1**. The adducts of methyl acetylenecarboxylate are unstable and decompose gradually at room temperature. Diphenylacetylene does not react with **1**.

The initial step of the reaction would be the electrophilic attack of the electron-deficient alkyne to the lone pair-electrons at the S atom. Between the two sulfur atoms in the ring, the electron-richer one should be attacked selectively. The S atom adjacent to C is electron-poorer than the S atom adjacent to N, because the π-electron density at the former S is lowered by the conjugation with the electron-attracting N atom.



The alkyne adducts of 1,2,5,3-cobaltadithiazole **3** are less stable than the alkyne adducts of 1,2,5-cobaltadithiolene. The adducts **3a** and **3b** react thermally and photochemically. The irradiation of **3** in a benzene solution with a medium pressure lamp brings about the migration of DMAD moiety and the eliminatio of benzonitrile to afford 3,4-dimethoxycarbonyl-1,2,5-cobaltadithiolene (**4**) (yield of **4a**, 70% and recovery of **3a**, 30% ; yield of **4b**, 60% and recovery of **3b**, 40% for 3 h irradiation).

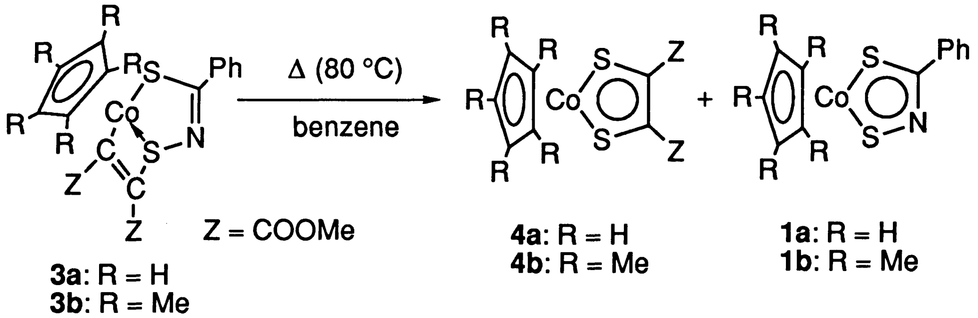


3a: R = H
3b: R = Me

4a: R = H
4b: R = Me

This photochemical behavior is different from that of the adduct between cobaltadithiolene and DMAD. study of the photoreaction of the adduct between (η^5-cyclopentadienyl)(1,2-dimethoxycarbonyl-1,2-ethylenedithiolato)cobalt(III) and deuterated DMAD revealed that the irradiation causes selectively the elimination of the alkyne moiety bridging between Co and S and no migration of the alkyne moiety.

In thermolysis in benzene under reflux, **3a** undergoes almost selectively the elimination of benzonitrile accompanied by the elimination of DMAD (yield of **4a**, 75%; yield of **1a**, trace; and recovery of **3a**, 26% for the thermolysis for 2 h), while **3b** undergoes the elimination of either DMAD or benzonitrile to give **1b** (56%) and **4b** (12%) in the thermolysis for 2 h (recovery of **3b**, 30%).



3a: R = H
3b: R = Me

4a: R = H
4b: R = Me

1a: R = H
1b: R = Me

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6) Adduct **3a**: mp 67-70 °C ; ^{1}H NMR ($CDCl_3$) δ = 3.67 (3H, s, $COOCH_3$), 3.90 (3H, s, $COOCH_3$), 5.23 (5H, s, Cp), 7.37 (3H, m, Ph), and 8.07 (2H, d, J = 7.4 Hz, Ph); ^{13}C NMR ($CDCl_3$) δ = 52.2 (OCH_3), 52.4 (OCH_3), 86.1 (Cp), 124.9 (S-$\underline{C}$-COOMe), 128.2 (Ph), 128.7 (Ph), 131.4 (Ph), 136.7 (Ph), 154.6 (S-C-$\underline{C}$OOMe), 170.6 (Co-C-$\underline{C}$OOMe), 172.2 (Co-$\underline{C}$-COOMe), and 204.3 (S-C-N); MS (70 eV) m/z (relative intensity) 330 (85, M$^+$-PhCN), 291 (19, M$^+$-DMAD), 277 (100), 246 (99), 188 (72, $CpCoS_2$), 124 (17, CpCo), 111 (11), 103 (78), and 59 (9).
Found: C, 49.78 ; H, 3.94; N, 3.12%. Calcd for $C_{18}H_{16}NO_4S_2Co$: C, 49.89; H, 3.72; N, 3.23%.
Adduct **3b**: mp 81-83 °C (dec); ^{1}H NMR ($CDCl_3$) δ = 1.68 (15H, s, Cp*), 3.65 (3H, s, $COOCH_3$), 3.85 (3H, s, $COOCH_3$), 7.33 (3H, m, Ph), and 8.11 (2H, d, J = 6.9 Hz, Ph); ^{13}C NMR ($CDCl_3$) δ = 9.1 ($C_5(\underline{C}H_3)_5$), 52.2 (OCH_3), 52.4 (OCH_3), 94.5 (($\underline{C}_5(CH_3)_5$), 124.5 (S-$\underline{C}$-COOMe), 127.7 (Ph), 128.4 (Ph), 130.9 (Ph), 137.1 (Ph), 155.3 (S-C-$\underline{C}$OOMe), 170.0 (Co-C-$\underline{C}$OOMe), 181.3 (Co-$\underline{C}$-COOMe), and 203.4 (S-C-N); MS (70 eV) m/z (relative intensity) 400 (61, M$^+$-PhCN), 361 (59, M$^+$-DMAD), 258 (100, Cp^*CoS_2), 133 (39) , 111(72), 103 (68, PhCN), and 59 (88, Co); FAB-MS m/z 504 (M+1); Found: C, 54.86; H, 5.20; N, 2.79%. Calcd for $C_{23}H_{26}NO_4S_2Co$: C, 54.86; H, 5.21; N, 2.78%.

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